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Ti-Rich Barrier Layer Self-Formed on Porous-Low-k Layers Using Cu(1 at.%Ti) Alloy Films

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ABSTRACT

To investigate applicability of the technique of barrier self-formation using Cu(Ti) alloy films on porous low-k dielectric layers, Cu(1at.%Ti) alloy films were deposited on porous SiOCH (low-k) dielectric layers in samples with and without about 6.5 nm-thick SiCN pore seals. Ti-rich barrier layers successfully self-formed on the porous low-k layer of both sample types after annealing in Ar for 2 h at 400-600°C. The Ti-rich barrier layers consisted of amorphous Ti oxides and polycrystalline TiC for the samples without pore sealing, and amorphous TiN, TiC and Ti oxides for the pore-sealed samples. The amorphous TiN originated from reaction of Ti atoms with the pore seal, and formed beneath the Cu alloy films. This may explain two peaks of Ti segregation at the interface that appeared on RBS profiles, and suggests that the Ti-rich barrier layers self-formed by the reaction of Ti atoms with the pore seal and porous low-k layers separately. The total molar amount of Ti atoms segregated at the interface in the pore-sealed samples was larger than that in the samples without pore sealing, resulting in lower resistivity. On the other hand, resistivity of the Cu alloy films annealed on the porous low-k layers was lower than that annealed on the non-porous low-k layers. Coarser Cu columnar grains were observed in the Cu alloy films annealed on the porous low-k layers, although the molar amount of Ti atoms segregated at the interface was similar in both sample types after annealing. The cause could be faster reaction of the Ti atoms with the porous dielectric layers.

Key words: Cu(Ti) alloy film; self-formation; diffusion barrier; porous low-k films; pore seal

INTRODUCTION

Cu interconnects have been used extensively in ULSI devices. However, large resistance-capacitance (RC) delay and poor device reliability have been critical issues as the device feature size has reduced to nanometer scale.[1] The large resistance increase is believed to be caused by small-grained Cu wires (numbers of grain boundaries) and large volume fraction of barrier layers in Cu wires.[2] Various methods have been reported to reduce the volume fraction of barrier layers in Cu wires, by fabricating a thin barrier layer.[3-11] One of the methods is a fabrication technique to prepare thin barrier layers in Cu(Ti)[6-9] or Cu(Mn)[10,11] alloy films by annealing at elevated temperatures. This technique using different alloy elements has already been reported, but high temperature annealing (>500°C) had been required.[12-17] We have succeeded in reducing the annealing temperature to 400°C when forming Ti-rich barrier layers using Cu(Ti) alloy films.[6] This is similar to the case using Cu(Mn) alloy films.

In our previous studies, supersaturated Cu(Ti) alloy films deposited on dielectric layers such as SiO_2, SiN, SiCO, SiCN, and SiOCH with low dielectric constants (low-k) were annealed at elevated temperatures, and thin Ti-rich layers were formed on the all the dielectric layers.[7,8] This is a unique case of the use of Cu(Ti) alloy films. The Ti-rich barrier layers were found to consist of polycrystalline TiN for the annealed Cu(Ti)/SiN samples,[7] and polycrystalline TiSi or TiC in addition to amorphous Ti oxides for other samples. The primary factor to control composition of the Ti-rich barrier layers was concluded to be the C concentration in the dielectric layers.[7,8] Crystalline TiC and TiSi were formed on the dielectric layers with a C concentration higher than 17 at.% and less than 14 at.%, respectively.[8]

For systematic investigation of the Ti-rich interface layer growth on dielectric layers

such as SiO_2, SiCO, SiCN, and SiOCH, the Rutherford backscattering spectrometry (RBS) technique was employed.[9] Although a few diffusion processes are possible, growth of the Ti-rich barrier layers was also found to be controlled by chemical reaction of the Ti atoms with the dielectric layers defined as

$$n = Z \cdot \exp(-E/RT) \cdot t^m, \quad (1)$$

where n is a molar amount of Ti atoms segregated to the interface, Z is a pre-exponential factor, and E is the activation energy for the reaction.[9]

Recently, porous low-k dielectrics have been used instead of dense low-k dielectrics to further reduce capacitance in Cu wires. In the present study, we tried to investigate applicability of the technique of barrier self-formation using Cu(Ti) alloy films on porous low-k dielectric layer, and clarify the mechanisms involved. The porous low-k dielectrics were used with or without pore seals, and thus we investigated effects of pores and pore sealing on self-formation of the Ti-rich barrier layers. The microstructures were analyzed by transmission electron microscopy (TEM) and Rutherford backscattering spectrometry (RBS), and correlated with the electrical properties of the Cu(Ti) films.

EXPERIMENTAL PROCEDURES

Cu(1 at.%Ti) alloy films were deposited on porous SiOCH (low-k) dielectric layers by a radio frequency magnetron sputtering technique. The porous low-k dielectric layers were grown on (100)-oriented Si wafers using conventional plasma chemical vapor deposition methods. Typical thickness was controlled to approximately 235 nm. In addition, about 6.5 nm-thick SiCN pore seals were deposited on some of the porous low-k layers. The dielectric constants (k) and compositions of these layers are shown in Table 1. Prior to film deposition, dust on the substrate surface was blown off using nitrogen gas.

The base pressure prior to deposition was approximately 1×10^{-6} Pa, and the sputtering power and working pressure were kept at 300 W and about 1 Pa, respectively. The substrate holder was placed 100 mm above the target. To prepare the Cu(Ti) films, small rectangular Ti plates were mounted on a Cu target. The purities of the Cu target and the Ti plates were 99.99% and 99.9%, respectively. The film thicknesses were measured using TEM and RBS: the typical thickness of the Cu(Ti) alloy films was controlled to approximately 360 nm. The samples were annealed in Ar isothermally at 400°C-600°C for 2 h. The electrical resistivity in the Cu(Ti) films was measured by a four-point probe method. The film microstructures were analyzed by X-ray diffraction (XRD) and TEM. The Ti segregation to the interface was investigated by RBS. For the RBS measurements, $^{4}He^{2+}$ ion beams with energy of 2 MeV were impinged perpendicularly onto the film surfaces. To identify composition and non-crystalline phases in the Ti-rich barrier layers, X-ray photoelectron spectroscopy (XPS) measurements and Ar etching were simultaneously carried out. To alleviate difficulties in the measurement of the very thin barrier layers, Ti concentration in the as-deposited Cu(Ti) alloy film was increased to 5 at.%, the typical thickness of the alloy films was controlled to approximately 70 nm, and annealing atmosphere was an ultra-high vacuum (UHV) to prevent Ti diffusion to the surface of the Cu alloy films.

To investigate effect of pores on the self-formation of Ti-rich barrier layers, Cu(1 at.%Ti) alloy films of about 440 nm thickness were simultaneously deposited on both porous and non-porous low-k (low-k1 and low-k4, see Table 1) dielectric layers, and simultaneously annealed in Ar isothermally at 400°C for 2h. The annealed samples were similarly analyzed using a four-point probe method, TEM, and RBS. In addition, to investigate effect of pores on growth of the self-formed Ti-rich barrier layers, first Cu(5

at.%Ti) alloy films of the same thickness and then TaN caps of about 50 nm thickness were deposited on the porous low-k dielectric layers. The TaN caps prevented Ti diffusion to the surface of the Cu alloy films during the annealing in Ar. The molar amounts of the Ti atoms segregated at the interface between the Cu alloy films and the porous low-k layers were estimated based on the RBS results.

RBS THEORY AND CRITERIA OF FIT

To obtain molar amounts of the Ti atoms segregated at the interface (n), the observed RBS intensities around the Ti peaks in the RBS profiles were fitted by the sum of the following components: Ti segregation at the interface, Ti atoms in the alloy film, and a Cu edge above the Ti segregation at the interface. The n value was estimated by dividing the number of Ti atoms in a unit of area (N) by Avogadro's number N_A, and the N value was estimated by dividing the peak area (A) of the Ti atoms in an RBS profile by the incident beam dose (Q), the scattering cross section of the element atom (σ), and the solid angle of the detector (Ω):[18]

$$n = N/N_A = A/(N_A Q \sigma \Omega), \quad (2)$$

where the values of Q, Ω, and σ of Ti atoms were 3.12×10^{13} (10 μC), 3×10^{-3} (steradians), and 6.28×10^{-29} m^2 (0.628 barns), respectively.

To obtain the A values originating in the Ti atoms segregated at the interface, the observed RBS intensities around the Ti peaks in the RBS profiles were fitted by the sum of three components: Ti segregation at the interface, Ti atoms in the alloy film, and a Cu edge above the Ti segregation at the interface (shown later in Fig. 3). The RBS profiles were adjusted through refinement of the parameters until the residual, $w_i(y_i(\text{obs}) - y_i(\text{calc}))^2$, was minimized in some sense, where $w_i = 1/y_i(\text{obs})$, $y_i(\text{obs})$ = observed intensity at the i-th

step, and y_i(calc) = calculated intensity at the i-th step. A best fit of the calculated pattern to the observed pattern was obtained on the basis of various indicators. One of the important indicators is the weighted pattern R index (R_{wp}), defined as

$$R_{wp} = \{\sum w_i(y_i(\text{obs}) - y_i(\text{calc}))^2 / \sum(w_i(y_i(\text{obs}))^2\}^{1/2}. \quad (3)$$

The numerator of the expression inside the braces is the sum of squared residuals and thus has expected value o-p, where o and p are the number of observations and the number of parameters, respectively. The expected R index, R_e (it is an adequate approximation for practical purpose), is accordingly defined as

$$R_e = \{o\text{-}p/\sum(w_i(y_i(\text{obs}))^2\}^{1/2}. \quad (4)$$

The ratio R_{wp}/R_e (=S) is a measure of how well the fitted model accounts for the data.[19] For example, an S value of 1.3 or less is usually considered to be quite satisfactory, whereas an S value of 1.7, on the other hand, is a probable warning that we should look further into the reasons and question the adequacy of our model.

RESULTS AND DISCUSSION

Self-Formation of Ti-Rich Barrier Layers on Porous Low-k Layers

Figure 1 shows RBS profiles of Cu(1at.%Ti)/porous-low-k samples before and after annealing in Ar for 2 h without (Fig. 1a) and with pore sealing (Fig. 1c). Ti peaks were obtained at the surface (Fig. 1b: Enlargement of areas around the Ti surface peaks shown in Fig. 1a) and interface after annealing at 400-600°C. This result was similar to those observed in Cu(Ti)/non-porous-dielectric samples after annealing at elevated temperature in Ar.[7,8] The Ti segregation at the surface indicates formation of Ti oxides produced by reaction of the Ti atoms with residual oxygen in Ar,[7,8] and that at the interface indicates self-formation of a Ti-rich barrier layer.[7-9] The Ti-peak intensities at both the surface and

interface increased with annealing temperature. Cu edges at the interface (around channel 600) remained sharp after annealing, indicating that Cu interdiffusion was prevented by the self-formed Ti-rich barrier layer. Thus, we demonstrated that the technique of barrier self-formation using Cu(Ti) alloy films works on the porous low-k dielectric layers with and without pore seals.

Figure 2 shows portions (around the Ti peaks at the interface) of the RBS profiles of the samples after annealing (Fig. 1). A single Ti peak was observed around channel 540 in the samples without pore sealing (Fig. 2a). This is similar to previous results for Cu(Ti)/dielectric-layer samples after annealing at elevated temperatures.[6-9] In contrast, Two Ti peaks were observed around channels 536 and 560 in the pore-sealed samples (Fig. 2b). Similar Ti peaks were observed in all pore-sealed samples after annealing at 400-600°C for 2 h. This suggests that two Ti-rich barrier layers self-formed by the reaction of Ti atoms with the pore-sealed (interface 1) and porous low-k (interface 2) layers separately.

Effect of Pore Seals on Molar Amounts of Ti atoms Segregated at the Interface, and Correlation with Electrical Resistivity

To obtain molar amounts of the Ti atoms segregated at the interface (n), the observed RBS intensities around the Ti peaks in the RBS profiles were fitted by the sum of the following components: Ti segregation at the interface, Ti atoms in the alloy film, and a Cu edge above the Ti segregation at the interface. Figure 3 shows typical fitting examples in the portions (around the Ti peaks at the interface) of the RBS profiles of the samples after annealing at 400°C for 2h (Fig. 1). Refinement plots (solid lines) were placed upon the observed data. The values of R_{wp} and S are described in Figures. 3a and b, and similar

values were obtained in fitting of RBS profiles observed in the other samples. This result indicates that the values obtained were low enough to support adequacy of the model.

Figure 4a shows variation of *n* value with annealing temperature. The *n* values increased with increasing annealing temperature. Note that total amounts of Ti atoms segregated at the interface in the pore-sealed samples were higher than those without pore sealing. In the pore-sealed samples, the *n* valus at interface 1 was smaller than that at interface 2, and the *n* values obtained at interface 1 after annealing at 400°C and 500°C were similar. This leads to the conclusion that the Ti segregation at interfaces 1 and 2 indicates reactions of Ti atoms with the 6.5 nm-thick pore-sealed (SiCN) and porous low-k layers, respectively. Sudden increase of the *n* value at interface 1 after annealing at 600°C may be caused by significant reaction of Ti atoms with both the pore-sealed and porous low-k layers, resulting in difficulty in distinguishing between the two layers. The resistivity of both the annealed pore-sealed samples and samples without pore sealing decreased with increasing annealing temperature. One of the reasons for the resistivity decrease is likely a decrease of residual Ti atoms in the Cu alloy films due to the reaction at the interface. Another reason is the formation of coarse Cu columnar grains, described below. Note that the resistivity of the pore-sealed samples was lower than that without pore sealing. This is attributed to lower residual Ti atoms in the alloy films (i.e., higher Ti segregation at the interface) in the pore-sealed samples. The low residual Ti atoms can also cause formation of coarse Cu columnar grains. This is in agreement with Cu columnar microstructures after annealing samples (Fig. 5).

Cross-sectional TEM images and a selected-area diffraction (SAD) pattern for Cu(1at.%Ti)/porous-low-k samples without pore sealing after annealing at 600°C in Ar for 2 h are shown in Figures 5a, b, and c, respectively. The cross-sectional TEM image

and SAD pattern for the annealed pore-sealed samples is shown in Figures 5d and e, for comparison. Figures 5a and d show distinct difference in Cu grain growth: fine columnar grains were observed in the samples without pore sealing (Fig. 5a) and coarse columnar grains in the pore-sealed samples (Fig. 5d). This can explain the resistivity difference in the annealed samples with and without pore sealing (Fig. 4b). The samples without pore sealing had a rough interface, indicating that Ti atoms reacted with the low-k layers at the pore surfaces (Fig. 5a). In contrast, the pore-sealed samples had a smooth interface (Fig. 5d). The Ti-rich barrier layers were very thin. A typical barrier layer in a portion of the samples without pore sealing is shown enlarged in Figure 5b, in which a Ti-rich barrier layer of about 10 nm thickness was observed. The barrier layer that formed on the pore-sealed samples was difficult to distinguish due to low contrast between the barrier layer and Cu alloy films at the same magnification. The SAD pattern for the sample without pore sealing shows that the Ti-rich barrier layer consisted of fine polycrystalline TiC (Fig. 5c). In contrast, no diffraction pattern except Cu was observed in the SAD pattern for the pore-sealed sample (Fig. 5e).

To identify composition and non-crystalline phases in the Ti-rich barrier layers, XPS measurements and Ar etching were simultaneously carried out. Figures 6a and b show depth dependence of composition of the Ti-rich barrier layers formed in samples without and with pore sealing, respectively. Ti-rich barrier layers were found to consist of TiC and Ti oxides in both samples, and TiN was found only in the pore-sealed sample. TiC and TiN were mainly formed beneath the Cu(Ti) alloy films. Some SAD patterns showed an orientation relationship between polycrystalline TiC and Cu grains in the annealed pore-sealed samples (not shown here). The amorphous TiN originated from reaction of Ti atoms with the pore seal, and formed beneath the Cu alloy films. This may

explain the two peaks of Ti segregation at the interface in the RBS profiles, and indicates that the Ti-rich barrier layers self-formed by the reaction of Ti atoms with the pore seal and porous low-k layers separately. Based on the XPS measurements and TEM observations, it was determined that the Ti-rich barrier layers consisted of polycrystalline TiC and amorphous Ti oxides in the samples without pore sealing, and of amorphous TiN, TiC and Ti oxides in the pore-sealed samples. The volume fraction of Ti oxides was large in the Ti-rich barrier layers.

The polycrystalline TiC was formed beneath the Cu(Ti) alloy films, and the C concentration of the porous low-k layer was 14.3 at.% (see Table 1). This is lower than that observed previously, wherein the crystalline TiC was formed on the dielectric layers with a C concentration higher than 17 at.%.[8] The C concentration of the porous low-k layers may still be in the region where the polycrystalline TiC can form. Not detecting formation of crystalline and amorphous TiSi is in agreement with the C concentration observed in the previous study.[8] The peak of Si-O was observed, but the peak appeared after the Ti-O peaks during Ar etching, and thus the Si-O peak was concluded to come from the porous low-k layers. Also, Si atoms were observed in the Cu alloy films after reaction of large amount of Ti atoms with dielectric layers (barrier layer thickness ~ 50 nm),[7,8] suggesting that Si atoms in the porous low-k layers do not form a Ti compound in the reaction. On the other hand, the annealed pore-sealed samples were observed to form amorphous TiN. The crystalline TiN formation was not detected in reaction of the Ti atoms with SiCN dielectric layers in the previous study,[8] which may be because the characterization methods such as TEM/SAD and secondary ion mass spectrometry used previously are not adequate to detect amorphous phases. Thus, reaction of Ti atoms with dielectric layers containing nitrogen can be concluded to form amorphous TiN phases.

However, there is some doubt as to whether crystalline or amorphous phases were formed in the samples with low concentration of C or N in dielectric layers. When we concluded formation of amorphous TiC or TiN, their volume fractions were small in the Ti-rich barrier layers. Thus, distinction between crystalline or amorphous status of Ti compounds is still difficult.

Effect of Pores on Self-Formation of Ti-Rich Barrier Layers

To understand effects of pores on self-formation of Ti-rich barrier layers, Cu(1at.%Ti) alloy films were simultaneously deposited on four types of low-k dielectric layers, and simultaneously annealed at 400°C in Ar for 2 h. The low-k dielectric layers were porous low-k (with and without pore sealing) and non-porous low-k (low-k1 and low-k4) types (see Table 1). Ti segregation was observed at the interface as well as the surface in all the samples (Fig. 7a). Resistivity for annealed Cu alloy films deposited on the porous low-k layers was lower than that on the non-porous low-k layers, although molar amounts of Ti atoms segregated at the interface were not significantly different in all the samples (Fig. 7b). Figure 8 shows cross-sectional TEM images for the annealed samples with the barrier layers formed on porous low-k and non-porous low-k layers. The annealed Cu alloy films deposited on the porous low-k layers exhibited coarser columnar grains (Fig. 8a) than those on the non-porous low-k layers (Fig. 8c), although the barrier layer thicknesses of both samples were not significantly different (Fig. 8b and d). The fine columnar grains remained in some places of the Cu alloy films deposited on the non-porous low-k layers (Fig. 7c). This is in agreement with lower resistivity of the Cu alloy films deposited on the porous low-k layers, although the molar amount of Ti atoms segregated at the interface was similar in the annealed samples deposited on both types of

dielectric layers.

To understand Cu grain growth difference between the annealed samples deposited on the porous and non-porous low-k layers, growth difference of the Ti-rich barrier layers on the porous and non-porous low-k layers was investigated. The initial Ti concentration in the Cu(Ti) alloy films deposited on the porous low-k layers without pore sealing was increased to 5 at.%, since the initial Ti concentration at 1 at.% was insufficient for analysis of growth parameters.[9] This was chosen to be the same Ti concentration as in the previous studies.[9] Figure 9a shows RBS profiles of Cu(5at.%Ti)/porous-low-k samples before and after annealing at 400°C in Ar. Ti peaks were obtained only at the interface after annealing (The TaN caps prevented Ti diffusion to a surface of the Cu alloy films during the annealing). The molar amounts of the Ti atoms segregated at the interface (n) was estimated from the A values of the Ti peaks at the interface of the RBS profiles (Fig. 9a). Plots of n versus annealing time (t) for the Cu(5 at.%Ti)/porous-low-k samples are shown in Figure 9b. For comparison, plots of n versus t for the Cu(5 at.%Ti)/low-k1 and Cu(5 at.%Ti)/SiO_2 samples are also shown in Figure 9b. There was an obvious contrast between annealing-time dependence of the n values for the Cu(5 at.%Ti)/porous-low-k samples and the other two samples. The n values for the Cu(5 at.%Ti)/porous-low-k samples increased to the saturated value within 2 h, although about 20 h was required for the other two samples. This suggests that the reaction of the Ti atoms with the porous low-k layers was much faster than those with non-porous dielectric layers. The faster reaction would quickly reduce the residual Ti atoms in the Cu alloy films, and thus Cu grain growth would start to occur at the beginning of the annealing. This is because the residual Ti atoms at the grain boundary are an obstacle to boundary migration (grain growth). The faster reaction of the Ti atoms with the porous low-k layers is attributed to an increase in

reaction area due to pores in the low-k layers.

CONCLUSIONS

Cu(1at.%Ti) alloy films were deposited on porous SiOCH (low-k) dielectric layers in samples with and without about 6.5 nm-thick SiCN pore seals. Self-formation of Ti-rich barrier layers was demonstrated on the porous low-k layer for both the samples after annealing in Ar for 2 h at 400-600°C. The Ti-rich barrier layers consisted of amorphous Ti oxides and polycrystalline TiC for the samples without pore sealing. Polycrystalline TiC was formed beneath the Cu alloy films. In the annealed pore-sealed samples, the Ti-rich barrier layers consisted of amorphous TiN, TiC and Ti oxides. The amorphous TiN originated from reaction of Ti atoms with the pore seal, and formed beneath the Cu alloy films. This may explain two peaks of Ti segregation at the interface that were observed in RBS profiles, and suggests that the Ti-rich barrier layers self-formed by the reaction of Ti atoms with the pore seal and porous low-k layers separately. The total molar amount of Ti atoms segregated at the interface in the pore-sealed samples was larger than that in the samples without pore sealing, resulting in lower resistivity. On the other hand, resistivity of the Cu alloy films annealed on the porous low-k layers was lower than that annealed on the non-porous low-k layers. Coarser Cu columnar grains were observed in the Cu alloy films annealed on the porous low-k layers, although the molar amount of Ti atoms segregated at the interface was similar in both sample types after annealing at 400°C for 2 h. This could result from faster reaction of the Ti atoms with the porous low-k layers because of increase in reaction area due to pores.

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REFERENCES

1. M.T. Bohr, and Y.A. El-Mansy, *IEEE Trans. Electron Devices* 45, 620 (1998).
2. M. Shimada, M. Moriyama, K. Ito, S. Tsukimoto and M. Murakami, *J. Vac. Sci. Technol.*, B24 190 (2006).
3. K. Numba, T. Ishigami, M. Enomoto, S. Kondo, H. Shinriki, D. Jeong, A. Shimizu, N.Saitoh, W-M. Li, S. Yamamoto, T. Kawasaki, T. Nakada and N. Kobayashi, Proc. Of AMC, 2006, p.269.
4. H. Wojcik, M. Friedemann, F. Feustelt, M. Albert, S. Ohsiekt, J. Metzgert, J. Voss, J.W. Bartha and C. Wenze, Proc. of IITC, 2007, p.19.
5. D. Jeong, H. Inoue and H. Shinriki, Proc. of IITC, 2008, p. 95.
6. S. Tsukimoto, M. Moriyama, K. Ito, and M. Murakami, *J. Electron. Mat.*, 34, 592-599 (2005).
7. K. Ito, S. Tsukimoto and M. Murakami, *Jpn. J. Appl. Phys.*, 46, 1942 (2007).
8. K. Kohama, K. Ito, S. Tsukimoto, K. Mori, K. Maekawa, and M. Murakami, *J. Electron. Mat.*, 37, 1148-1157 (2008).
9. K. Kohama, K. Ito, K. Mori, K. Maekawa, Y. Shirai and M. Murakami, *J. Electron. Mat.*, 38, 1913-1920 (2009).
10. J. Koike and M. Wada, *Appl. Phys. Lett.*, 87, 041911 (2005).
11. T. Usui, K. Tsumura, H. Nasu, Y. Hayashi, G. Minamihaba, H. Toyoda, S. Ito, H. Miyajima, K. Watanabe, M. Shimada, A. Kojima, Y. Uozumi and H. Shibata, Proc. of IITC, 2005, p. 188.
12. P.J. Ding, W.A. Lanford, S. Hymes, and S.P. Murarka, *J. Appl. Phys.* 75, 3627 (1994).
13. D. Adams, T.L. Alford, N.D. Theodore, S.W. Russell, R.L. Spreitzer, and J.W. Mayer, *Thin Solid Films* 262, 199 (1995).

14. C.J. Liu, and J.S. Chen, *Appl. Phys. Lett.* 80, 2678 (2002).

15. C.J. Liu, J.S. Jeng, J.S. Chen, and Y.K. Lin, *J. Vac. Sci. Technol.* B 20, 2361 (2002).

16. M.J. Frederick, R. Goswami, and G. Ramanath, *J. Appl. Phys.* 93, 5966 (2003).

17. M.J. Frederick, and G. Ramanath, *J. Appl. Phys.* 95, 3202 (2004).

18. W.-K. Chu, J.W. Mayer, and M.-A. Nicolet, Backscattering Spectrometry, San Diego : Academic Press, 1978, pp. 91-92.

19. R.A. Young, The Rietveld Method, New York : Oxford University Press, 1993, pp. 22.

Table 1 Dielectric constants (*k*) of the porous low-k dielectric layers and their C, O, Si, and H concentrations (at.%), together with those of low-k1 and low-k4 dielectric layers, for comparison.

Dielectric layers	*k*	C (at.%)	O (at.%)	Si (at.%)	H (at.%)
Porous low-k	2.5	14.3	30.7	18.2	36.9
Low-k1	3.0	18.8	24.6	18.5	38.1
Low-k4	2.6	13.3	29.9	17.7	39.1

Figure legends

Fig. 1 RBS profiles of the Cu(1 at.%Ti)/porous-low-k samples before and after annealing in Ar for 2 h (a) without and (c) with pore sealing. Areas around the Ti surface peaks in (a) are enlarged in (b). Annealing temperature range was from 400°C to 600°C.

Fig. 2 Portions around the Ti peaks at the interface of the RBS profiles of Cu(1 at.%Ti)/porous-low-k samples after annealing in Ar for 2 h (a) without and (b) with pore sealing. Annealing temperature range was from 400°C to 600°C.

Fig. 3 Portions around the Ti peaks at the interface of the RBS profiles of Cu(1 at.%Ti)/porous-low-k samples after annealing in Ar for 2 h at 400°C (a) without and (b) with pore sealing. Refinement plots (solid line) are placed upon the observed data (□). The refinement plots consisted of three components: Ti segregation at the interface, Ti atoms in the alloy film, and a Cu edge above the Ti segregation at the interface.

Fig. 4 (a) Molar amounts of Ti atoms segregated at the interface estimated from the Ti peaks at the interface in the RBS profiles and (b) resistivity in the Cu(1at.%Ti)/porous-low-k samples after annealing in Ar for 2 h with and without pore sealing. Annealing temperature range was from 400°C to 600°C.

Fig. 5 (a, b) Cross-sectional TEM images and (c) a SAD pattern for Cu(1at.%Ti)/porous-low-k samples without pore sealing after annealing at 600°C in Ar for 2 h. (b) Enlarged TEM images of a portion around the Cu(1at.%Ti)/porous-low-k

interface. For comparison, (d) a cross-sectional TEM image and (e) a SAD pattern for the annealed pore-sealed samples.

Fig. 6 Depth dependence of the composition of Ti-rich barrier layers self-formed at the interface of Cu(5at.%Ti)/porous-low-k samples (a) without and (b) with pore sealing.

Fig. 7 (a) RBS profiles and (b) resistivities and molar amounts of Ti atoms segregated at the interface for the Cu(1at.%Ti)/dielectric-layer samples after annealing. The Cu(Ti) alloy films were simultaneously deposited on four types of low-k dielectric layers, and annealed in Ar for 2 h at 400°C. The low-k dielectric layers were porous low-k (with and without pore sealing) and non-porous low-k (low-k1, and low-k4).

Fig. 8 Cross-sectional TEM images and for (a) the Cu(1at.%Ti)/porous-low-k sample without pore sealing and (c) the Cu(1at.%Ti)/low-k1 sample after annealing in Ar for 2 h at 400°C. These are the same samples as those shown in Figure. 7. Enlarged TEM images of a portion around the Cu(1at.%Ti)/dielectric-layer interface for (b) the Cu(1at.%Ti)/porous-low-k sample without pore sealing and (d) the Cu(1at.%Ti)/low-k1 sample.

Fig. 9 (a) RBS profiles or the Cu(5at.%Ti)/porous-low-k samples after annealing in Ar at 400°C. (b) Annealing-time dependence of molar amounts of Ti atoms segregated at the interface estimated the Ti peaks at the interface in the RBS profiles (a). For comparison, annealing-time dependence of molar amounts of Ti atoms segregated at the interface of the Cu(5at.%Ti)/low-k1 and Cu(5at.%Ti)/SiO_2 samples were plotted together in (b). These

were reported in the previous paper. [9]

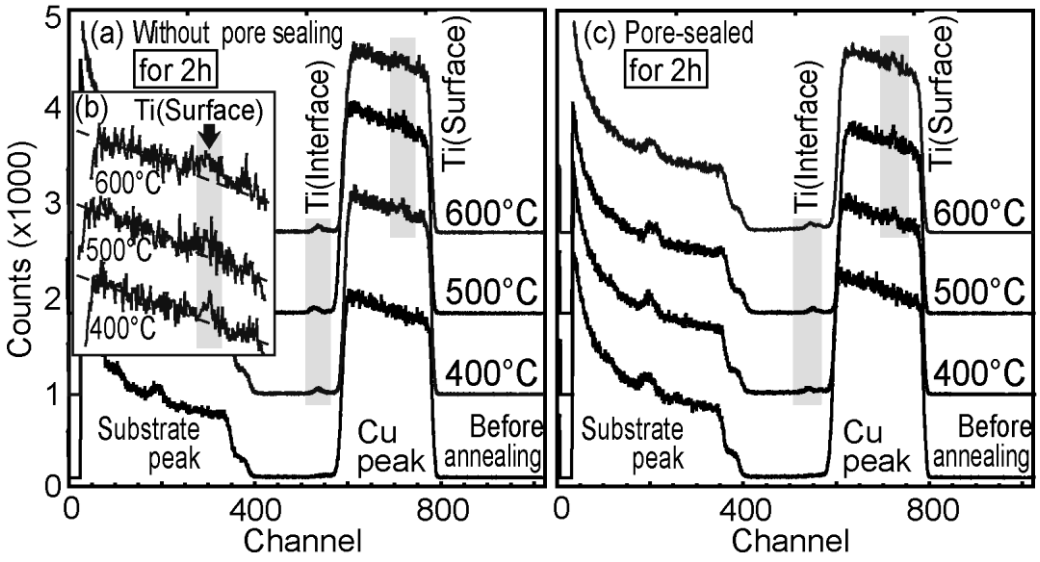
(a) Without pore sealing
for 2h
(b) Ti(Surface)
600°C
500°C
400°C
Ti(Interface)
Ti(Surface)
600°C
500°C
400°C
Substrate peak
Cu peak
Before annealing
(c) Pore-sealed
for 2h
Counts (x1000)
Channel

Fig. 1

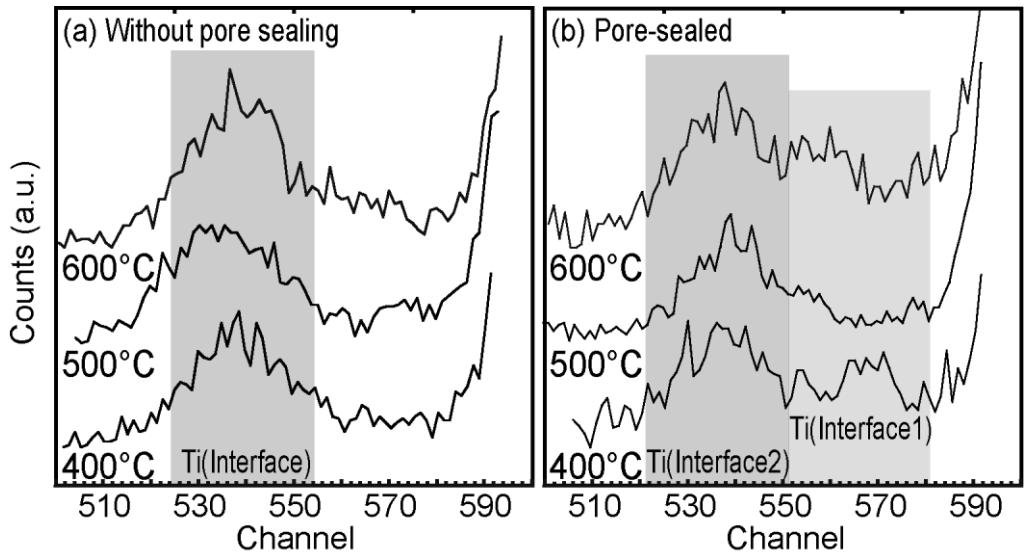
(a) Without pore sealing
(b) Pore-sealed
600°C
500°C
400°C
Ti(Interface)
Ti(Interface1)
Ti(Interface2)
Counts (a.u.)
Channel

Fig. 2

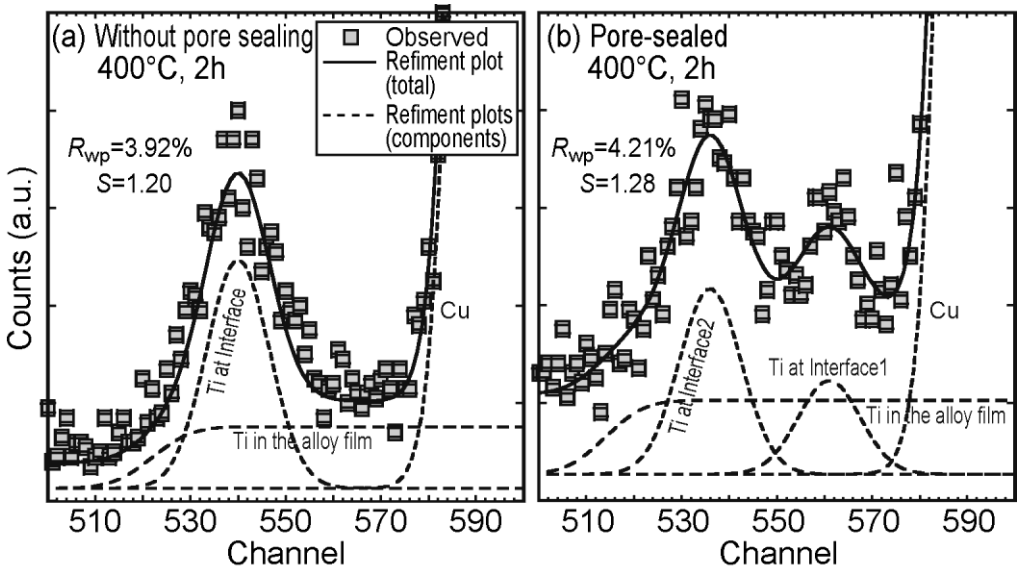
(a) Without pore sealing
400°C, 2h
Observed
Refiment plot (total)
Refiment plots (components)
R_{wp}=3.92%
S=1.20
Ti at Interface
Cu
Ti in the alloy film
(b) Pore-sealed
400°C, 2h
R_{wp}=4.21%
S=1.28
Ti at Interface2
Ti at Interface1
Cu
Ti in the alloy film
Counts (a.u.)
510 530 550 570 590
Channel
510 530 550 570 590
Channel

Fig. 3

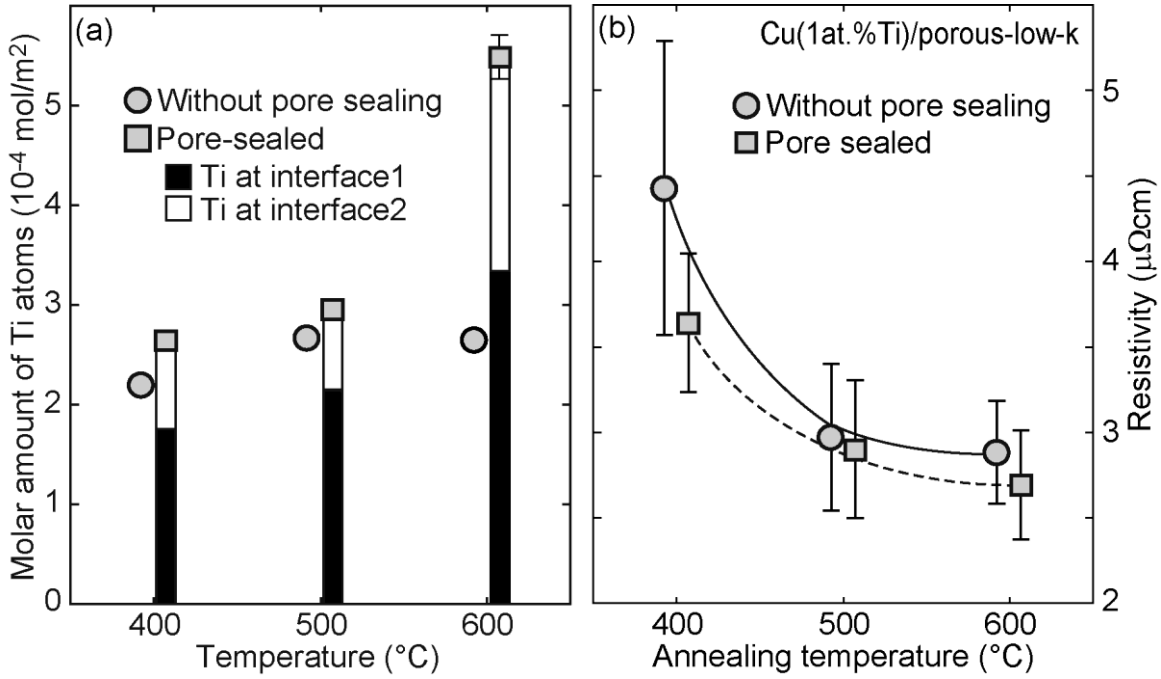
(a)
Without pore sealing
Pore-sealed
Ti at interface1
Ti at interface2
Molar amount of Ti atoms (10^{-4} mol/m^2)
0 1 2 3 4 5
400 500 600
Temperature (°C)
(b)
Cu(1at.%Ti)/porous-low-k
Without pore sealing
Pore sealed
Resistivity (μΩcm)
2 3 4 5
400 500 600
Annealing temperature (°C)

Fig. 4

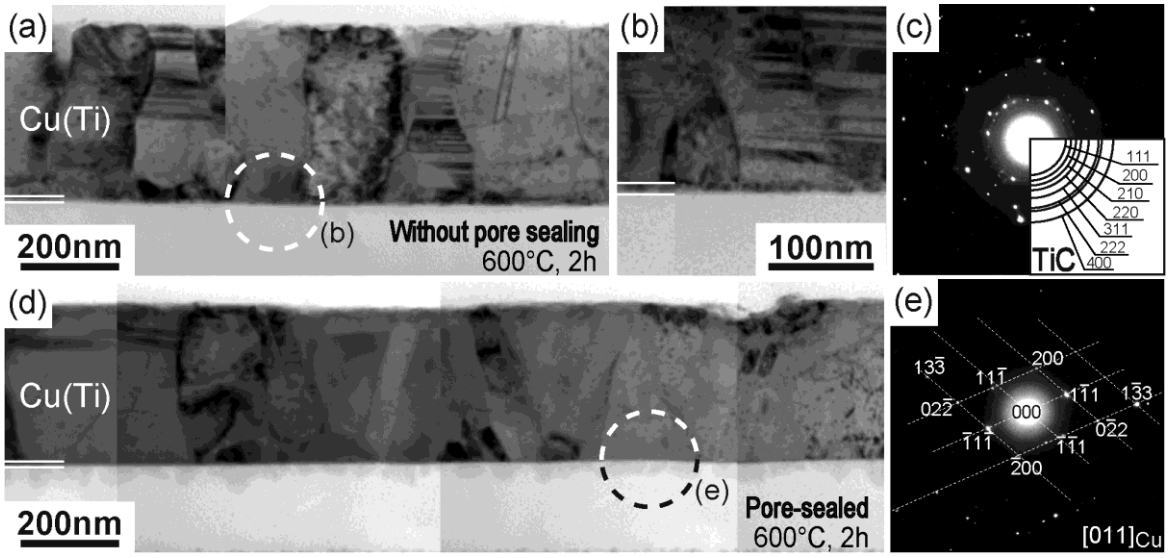
(a)
Cu(Ti)
200nm
(b)
Without pore sealing
600°C, 2h
(b)
100nm
(c)
111
200
210
220
311
222
400
TiC
(d)
Cu(Ti)
200nm
(e)
Pore-sealed
600°C, 2h
(e)
200
000
[011]Cu

Fig. 5

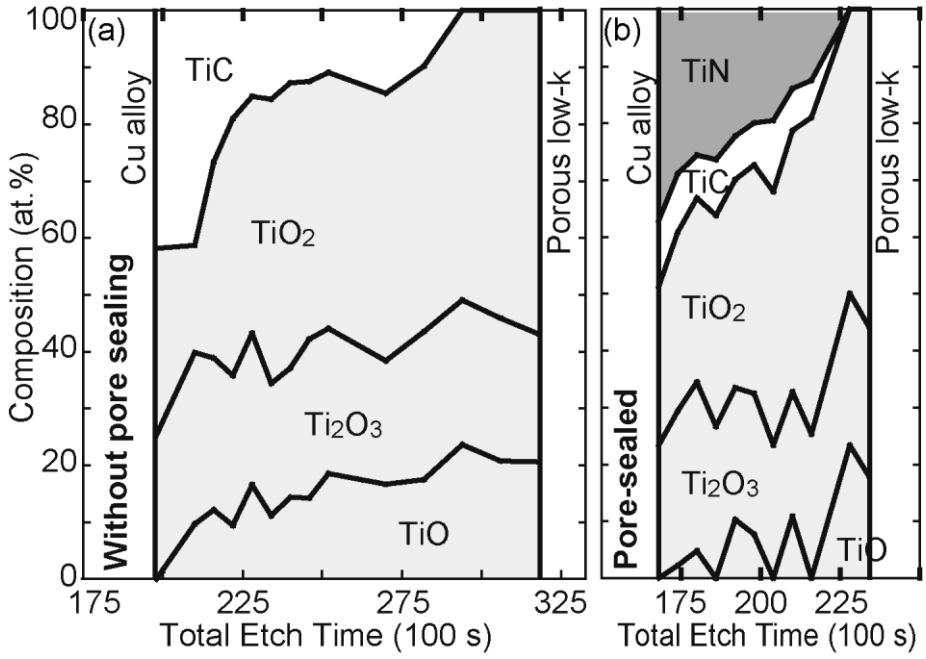
(a)
Cu alloy
TiC
TiO2
Ti2O3
TiO
Porous low-k
Without pore sealing
Composition (at.%)
Total Etch Time (100 s)
(b)
Cu alloy
TiN
TiC
TiO2
Ti2O3
TiO
Porous low-k
Pore-sealed
Total Etch Time (100 s)

Fig. 6

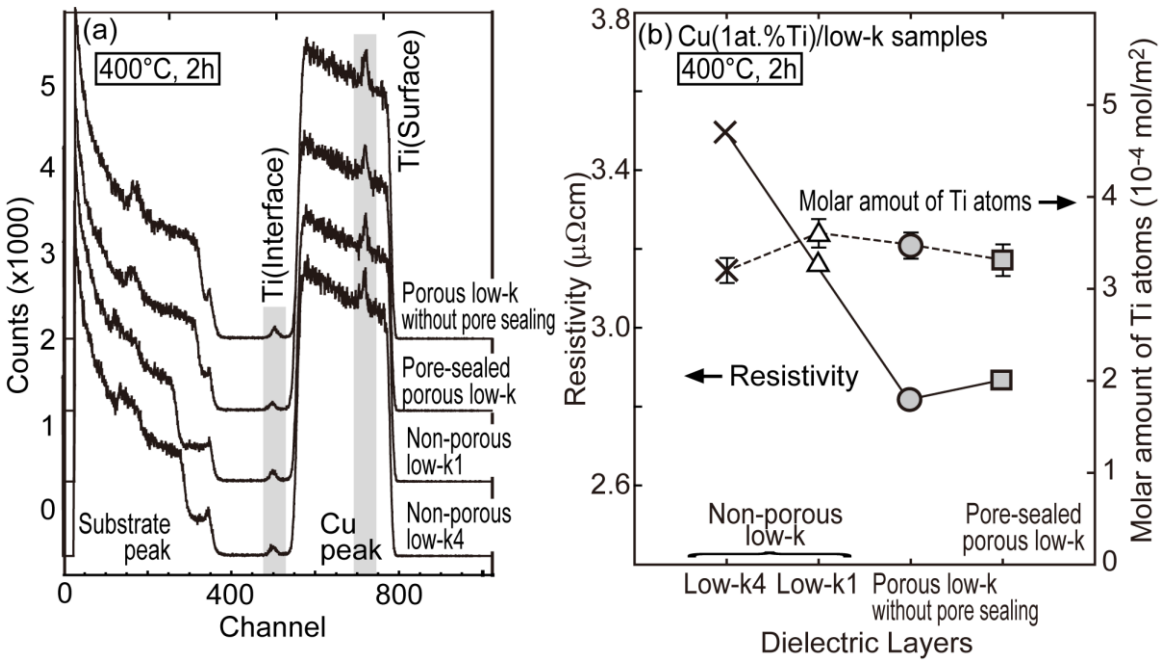
(a)
400°C, 2h
Counts (x1000)
Ti(Interface)
Ti(Surface)
Porous low-k without pore sealing
Pore-sealed porous low-k
Non-porous low-k1
Non-porous low-k4
Substrate peak
Cu peak
Channel
(b) Cu(1at.%Ti)/low-k samples
400°C, 2h
Resistivity (μΩcm)
Molar amout of Ti atoms
Resistivity
Molar amount of Ti atoms (10-4 mol/m2)
Non-porous low-k
Pore-sealed porous low-k
Low-k4
Low-k1
Porous low-k without pore sealing
Dielectric Layers

Fig. 7

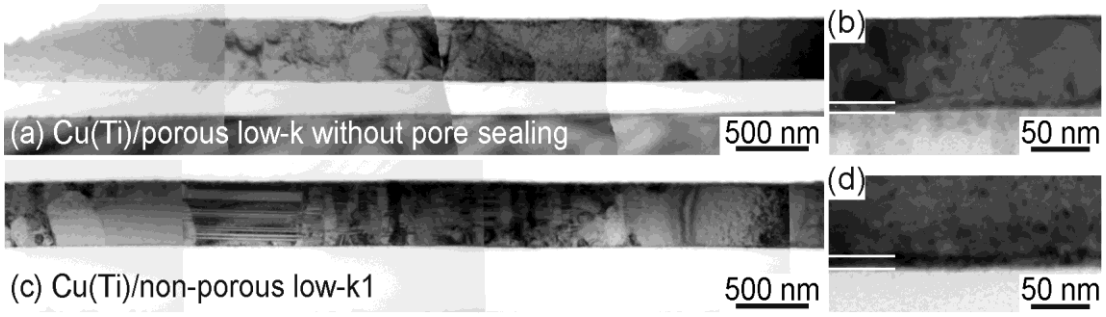
(a) Cu(Ti)/porous low-k without pore sealing
500 nm
(b)
50 nm
(c) Cu(Ti)/non-porous low-k1
500 nm
(d)
50 nm

Fig. 8

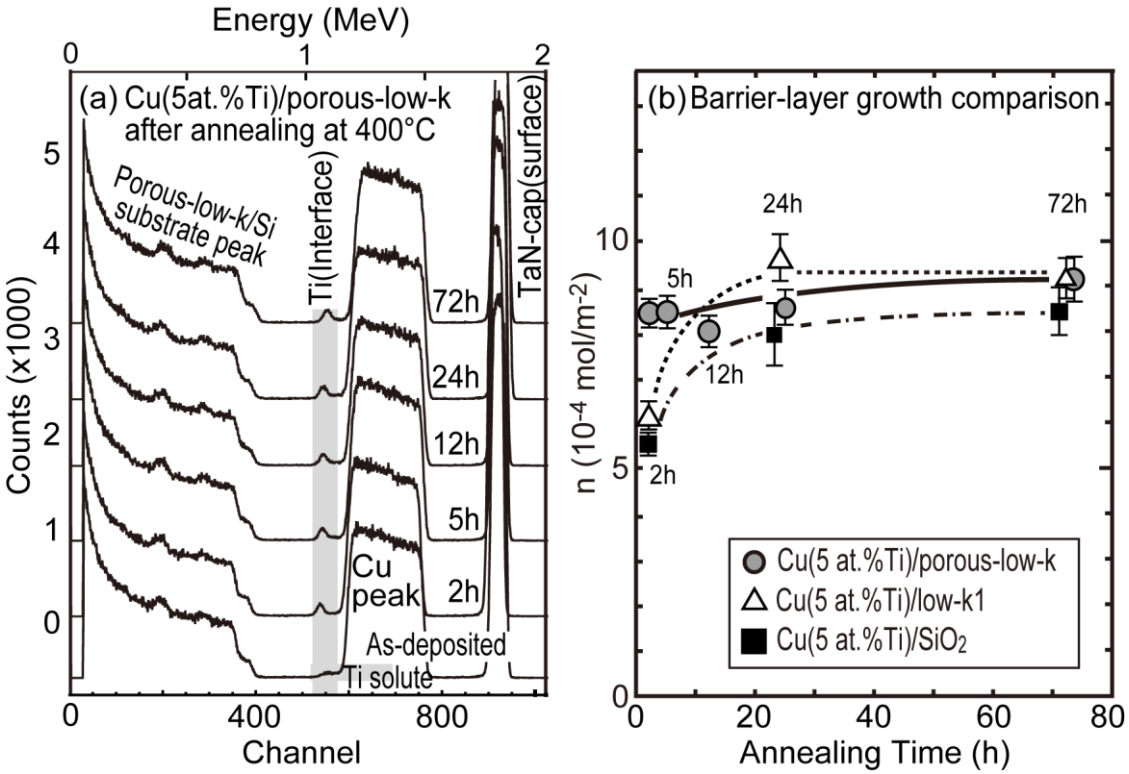
Energy (MeV)
0
1
2
(a) Cu(5at.%Ti)/porous-low-k
after annealing at 400°C
Porous-low-k/Si
substrate peak
Ti(Interface)
TaN-cap(surface)
72h
24h
12h
5h
2h
Cu
peak
As-deposited
Ti solute
Counts (x1000)
Channel
(b) Barrier-layer growth comparison
n (10-4 mol/m-2)
Annealing Time (h)
Cu(5 at.%Ti)/porous-low-k
Cu(5 at.%Ti)/low-k1
Cu(5 at.%Ti)/SiO2

Fig. 9